Benzene &
Aromatic Compound

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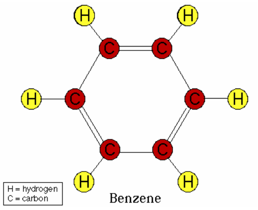
Learning outcome

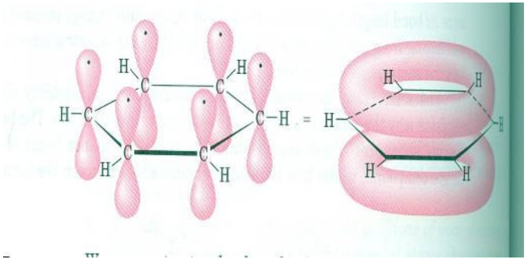
- Structure of benzene
- Characteristic of benzene
- Naming of benzene
- Reaction of benzene
    - ☐ Electrophile addition
    - ☐ Effect of substituents on reactivity
    - ☐ Relative reactivity of substituents benzene
    - ☐ Effect of substituent on orientation
    - ☐ Synthesis of aromatic compound

Structure of Benzene

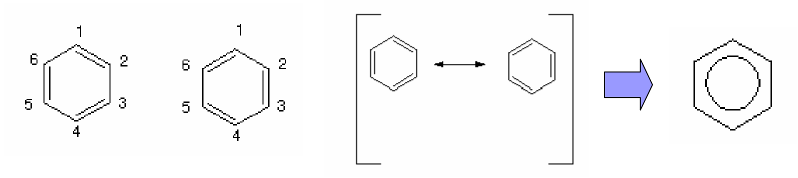
- Definition of ‘Aromatic Compounds’

  ‘Cyclic compounds that having some number of conjugated double bonds and unusually large resonance energy’
- The opposite of aromatic is aliphatic.
- Molecular formula: C_6H_6
- It is with 6-membered cyclic structure with 3 conjugated double bond.
- Benzene is a ring with all of sp^2 hybrid C atoms with unhybridized orbital P orbital are aligned perpendicular to the ring.





- The conjugated double bond are constantly moving due to resonances. Hence the structure is usually drawn as:



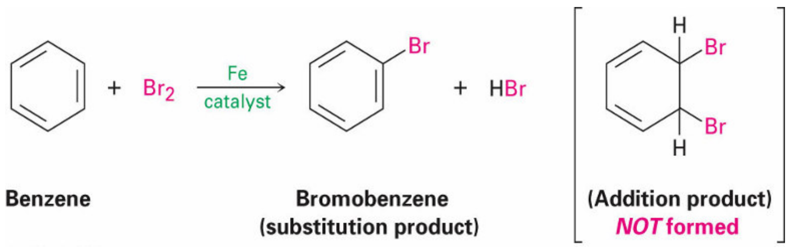
- The difference is that in A, the double bonds are between C1-C2, C3-C4, and C5-C6, whereas in B the double bond positions are C2-C3, C4-C5, and C6-C1.
- In the real molecule benzene, none of the bonds are double bonds and none are single, all six bonds are equivalent and are intermediate between double and single.
- resonance structures: the possible of moving of pi bonding in benzene.

Physical Properties

- Melting points: More symmetrical than corresponding alkane, pack better into crystals, so higher melting points.
- Boiling points: Dependent on dipole moment, so *ortho* > *meta* > *para*, for disubstituted benzenes.
- Density: More dense than non-aromatics, less dense than water.
- Solubility: Generally insoluble in water.

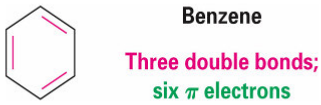
Stability of Benzene

- Benzene is much less reactive than typical alkene and fails to undergo the usual alkene reactions. Thus it is a very stable structure.
  - ☐ Cyclohexene reacts rapidly with Br_2 and gives the *addition* product 1,2-dibromocyclohexane
  - ☐ Benzene reacts only slowly with Br_2 and gives the *substitution* product C_6H_5Br

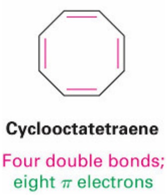


Characteristic of Aromatic Compounds

- It must be cyclic
- It must be having the same number of conjugated π bonding
- It must be flat so that the *p* orbital overlap can occur. Planar structure
- The delocalisation of π electron must lower the electronic energy.
- It must fulfill Huckel's rule, having (4n + 2 pi) electrons; whereby n=0 or any positive number (n=0,1,2,3,…). Hence, with this rule, rings which has pi electrons =2,6,10,14 are aromatic ring.



4n+2=(4x1)+2
=6

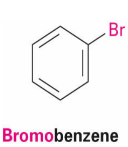


4n+2=(4x1)+2=6
hence, it is not aromatic as the ring has 8 pi e.
Non-aromatic

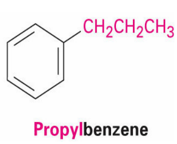
Naming Aromatic Compounds 1. Monosubstituted Benzenes

Aromatic substances have acquired nonsystematic names

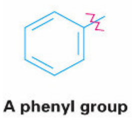
- Nonsystematic names are discouraged but allowed by IUPAC.
- It is derivative of benzene.
- Substituent name is written as though they were attached.
- In some case, benzene ring become substituent. Alkyl substituent larger than the ring (7 or more carbons), named as a phenyl-substituted alkane or when the chain is priority.



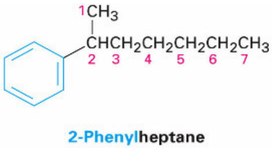
Bromobenzene



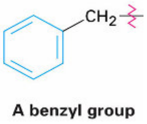
Propylbenzene



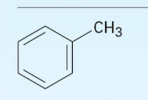
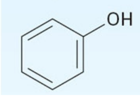
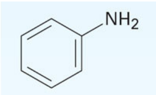
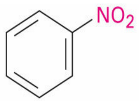
A phenyl group



2-Phenylheptane

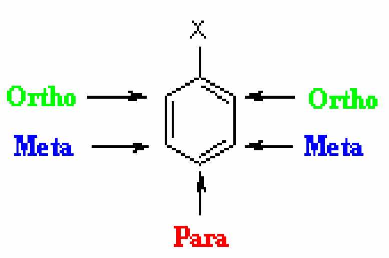


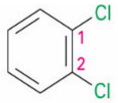
A benzyl group

				
Common	Toluene	Phenol	Aniline	Nitrobenzene
IUPAC	Methylbenzene	Hydroxybenzene	Aminobenzene	Nitrobenzene

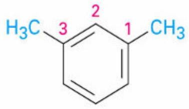
Disubstituted benzenes

- Named using one of the prefixes
  1. *ortho-* (*o-*)
     - Ortho-disubstituted benzene has two substituents in a 1,2 relationship
  2. *meta-* (*m-*)
     - Meta-disubstituted benzene has its substituents in a 1,3 relationship
  3. *para-* (*p-*)
     - Para-disubstituted benzene has its substituents in a 1,4 relationship

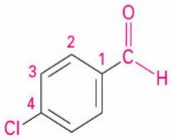




***ortho*-Dichlorobenzene**
1,2 disubstituted



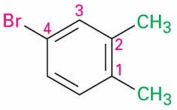
***meta*-Dimethylbenzene**
(*meta*-xylene)
1,3 disubstituted



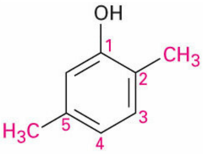
***para*-Chlorobenzaldehyde**
1,4 disubstituted

Benzenes with more than two substituents

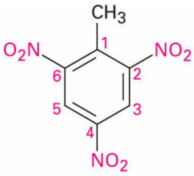
- Named by numbering the position of each so that the lowest possible numbers are used
- The substituents are listed alphabetically when writing the name
- Any of the monosubstituted aromatic compounds can serve as a parent name, with the principal substituent (-OH in phenol or $–CH_3$ in toluene) attached to C1 on the ring.
- Benzene compounds that contain three or more substituents are always named by the number system. In this system, numbers are assigned to substituents so that the substituents have the lowest possible combination of numbers.



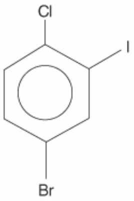
4-Bromo-1,2-dimethylbenzene



2,5-Dimethylphenol



2,4,6-Trinitrotoluene (TNT)

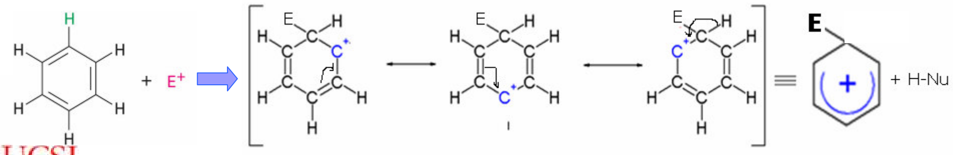


1-chloro-2-iodo-4-bromobenzene
(not 1-bromo-3-iodo-4-chlorobenzene)

Reactions of Aromatic Compounds: Electrophilic Substitution

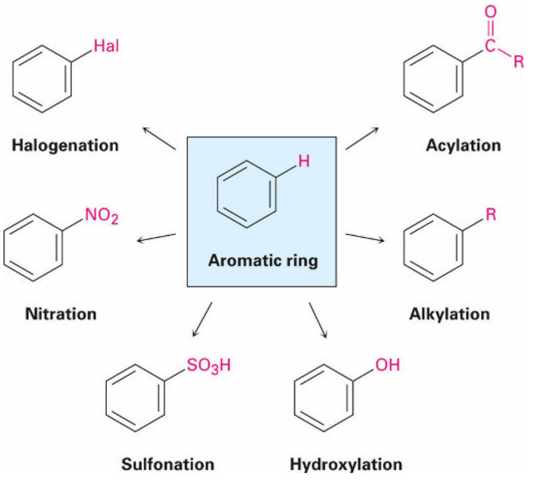
Electrophilic aromatic substitution

- A process in which an electrophile (E^+) reacts with an aromatic ring and substitutes for one of the hydrogens.
- Aromatic undergo this rxn due to being very stable and has large number of delocalized pi e.
- This reaction is characteristic of all aromatic rings.
- The mechanism involves 2 steps:
  - **1ST STEP**: attack on E+ by pi e of aromatic ring to form carbocation (benzonium ion)
  - Benzonium ion has 3 resonance structure which delocalize the +ve charge around the aromatic ring. (a nucleophile cant add in to form new product as it will lost the aromaticity of the ring.)
  - **2ND STEP**: carbocation react with nucleophile to form an additional product.



Reactions of Aromatic Compounds: Electrophilic Substitution

- Many substituents can be introduced onto an aromatic ring through electrophilic substitution reactions
  - Halogen (-Cl, -Br, -I)
  - Nitro group (-NO_2)
  - Sulfonic acid group (-SO_3H)
  - Hydroxyl group (-OH)
  - Alkyl group (-R)
  - Acyl group (-COR)

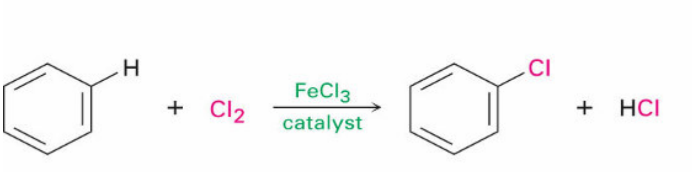


Electrophilic Aromatic Substitution Reaction

i) Halogenation

Electrophilic aromatic substitution reaction begins in a similar way to electrophilic alkene addition reaction

- $FeBr_3$ catalyst is needed for bromination of benzene to occur
  - $FeBr_3$ polarizes Br_2 molecule making it more electrophilic
  - Polarization makes $FeBr_4^-Br^+$ species that reacts as if it were Br^+
    - The polarized Br_2 molecule reacts with the nucleophilic benzene ring to yield a nonaromatic carbocation intermediate which is doubly allylic and has three resonance forms



- **Chlorination proceeds by a similar mechanism.**

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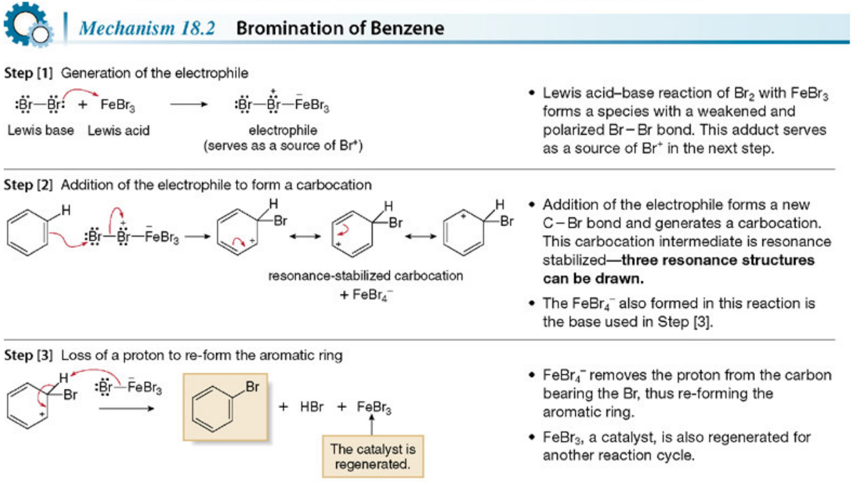


Mechanism 18.2 **Bromination of Benzene**

Step [1] Generation of the electrophile

- Lewis acid–base reaction of Br_2 with $FeBr_3$ forms a species with a weakened and polarized Br – Br bond. This adduct serves as a source of Br^+ in the next step.

Step [2] Addition of the electrophile to form a carbocation

- Addition of the electrophile forms a new C – Br bond and generates a carbocation. This carbocation intermediate is resonance stabilized—**three resonance structures can be drawn.**
- The $FeBr_4^-$ also formed in this reaction is the base used in Step [3].

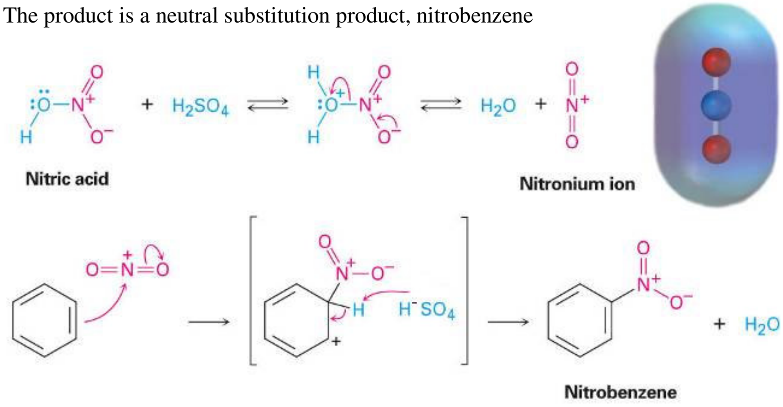
Step [3] Loss of a proton to re-form the aromatic ring

- $FeBr_4^-$ removes the proton from the carbon bearing the Br, thus re-forming the aromatic ring.
- $FeBr_3$, a catalyst, is also regenerated for another reaction cycle.

Electrophilic Substitution *ii) Nitration*

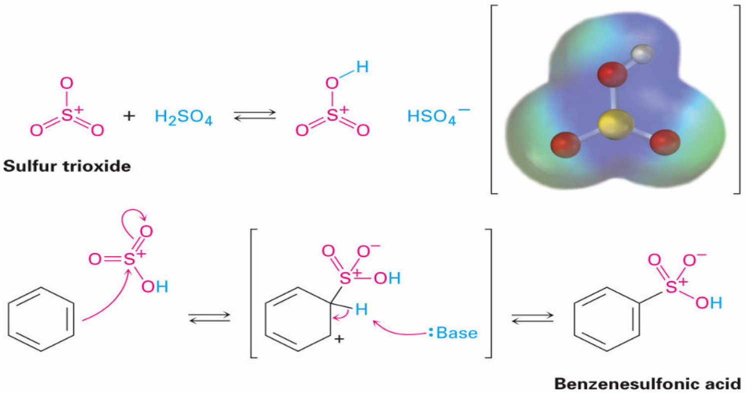
Aromatic rings can be nitrated with a mixture of concentrated nitric and sulfuric acids

- ☐ The electrophile is the nitronium ion, NO^{2+} which is generated from HNO_3 by protonation and loss of water
- ☐ The nitronium ion reacts with benzene to yield a carbocation intermediate, and loss of H^+
- ☐ The product is a neutral substitution product, nitrobenzene



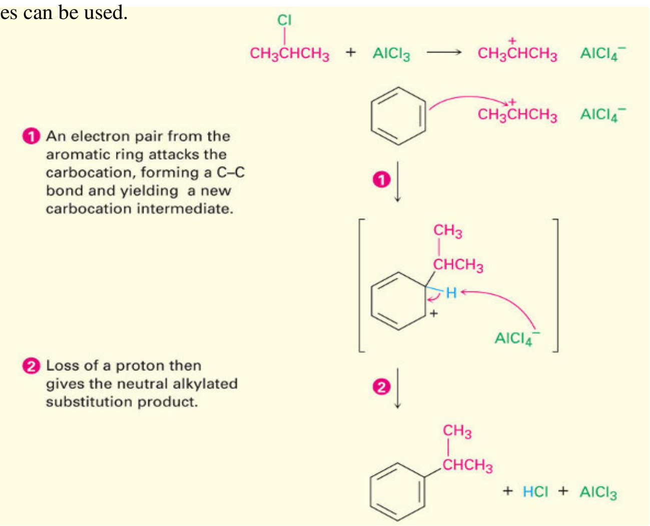
Electrophilic Substitution *iii) Sulfonation*

- Aromatic rings can be sulfonated in the laboratory by reaction with fuming sulfuric acid, a mixture of H_2SO_4 and SO_3
  - ☐ The reactive electrophile is either HSO_3^+ or neutral SO_3
  - ☐ Substitution occurs by the same two-step mechanism seen for bromination and nitration
- Aromatic sulfonation does not occur naturally
- Aromatic sulfonation is widely used in the preparation of dyes and pharmaceutical agents



iv) Friedel-Crafts Alkylation of Aromatic Rings

- The electrophile is a carbocation, generated by $AlCl_3$-assisted dissociation of an alkyl halide. Only *alkyl* halides can be used.

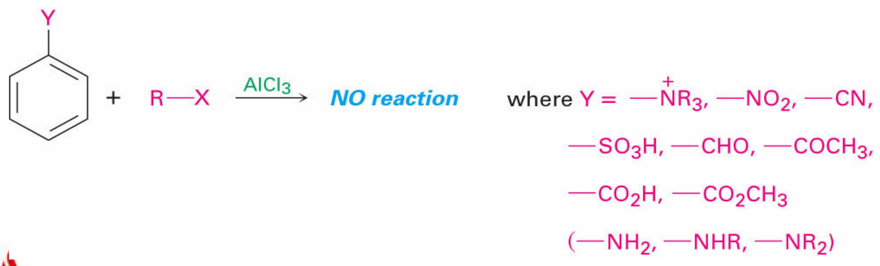


① An electron pair from the aromatic ring attacks the carbocation, forming a C–C bond and yielding a new carbocation intermediate.

② Loss of a proton then gives the neutral alkylated substitution product.

Alkylation

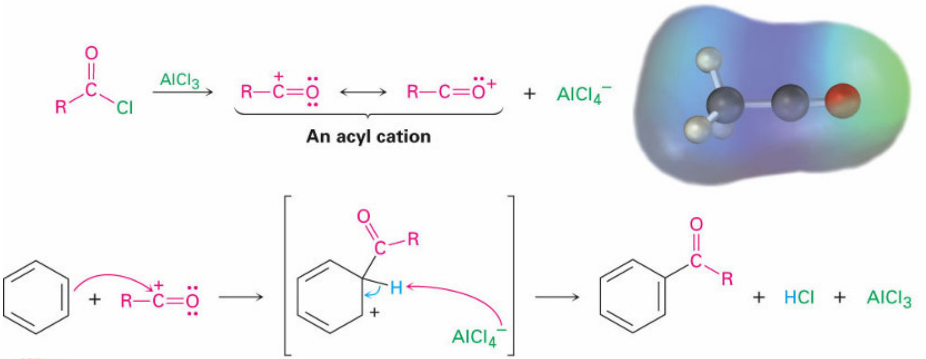
2. Friedel-Crafts reactions do not succeed on aromatic rings that are substituted either by a strongly electron-withdrawing group such as carbonyl (C=O) or by an amino group ($-NH_2$, NHR, $-NR_2$)
   - The presence of a substituent group already on a ring can have a dramatic effect on that ring’s subsequent reactivity toward further electrophilic substitution



v) Friedel-Craft Acylation of Aromatic Rings

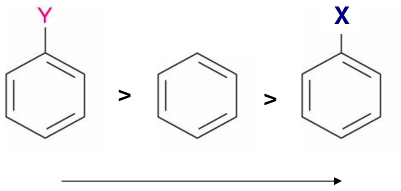
An aromatic ring is *acylated* by reaction with a carboxylic acid chloride, RCOCl, in the presence of $AlCl_3$

- An acyl group is substituted onto an aromatic ring
  - ☐ The reactive electrophile is a resonance-stabilized acyl cation
    - An acyl cation is stabilized by interaction of the vacant orbital on carbon with lone-pair electrons on the neighboring oxygen
  - ☐ Because of stabilization, no carbocation rearrangement occurs during acylation



The Effects of Substituent on Reactivity

- Different substituents exerts different effect toward the aromatic ring.
- 2 groups of substituents
  - ☐ E donating
  - ☐ E withdrawing

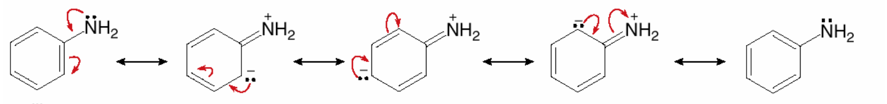


Reactivity decrease

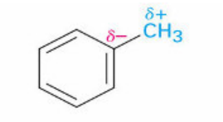
Y= E donating species
X = E withdrawing species

Electron Donating Species

- Electron-donating groups stabilize the carbocation, making the reaction faster.
- Donation of electron density to the ring makes benzene more electron rich.
- Polarizable alkyl groups donate electron density, and thus exhibit an electron-donating inductive effect.
- **An electron-donating resonance effect is observed whenever an atom Z having a lone pair of electrons is directly bonded to a benzene ring.**
- A resonance effect is electron donating when resonance structures place a negative charge on carbons of the benzene ring.

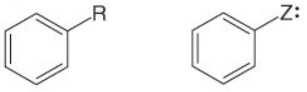


Three resonance structures place a (–) charge on atoms in the ring.



Inductive electron donation

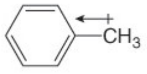
Electron-donating groups



R = alkyl Z = N or O

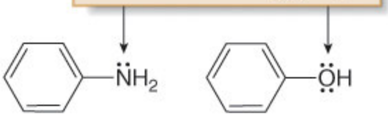
Common electron-donating groups:
- Alkyl groups
- Groups with an N or O atom bonded to the benzene ring; N or O must have a lone pair.

Electron-donating inductive effect



- Alkyl groups are **polarizable,** making them electron-donating groups.

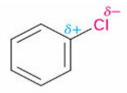
Electron-donating groups



The electron-donating resonance effect predominates.

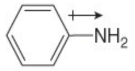
Electron Withdrawing Species

- Withdrawal of electron density from the ring makes benzene less electron rich.
- Atoms more electronegative than carbon—including N, O, and X—pull electron density away from carbon and thus exhibit an electron-withdrawing inductive effect.
- A resonance effect is electron withdrawing when resonance structures place a positive charge on carbons of the benzene ring.
- Electron-withdrawing groups destabilize the carbocation, making the reaction slower.



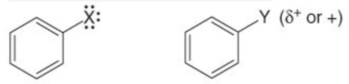
Inductive electron withdrawal

Electron-withdrawing inductive effect



- N is **more electronegative** than C.
- N inductively withdraws electron density.

Electron-withdrawing groups

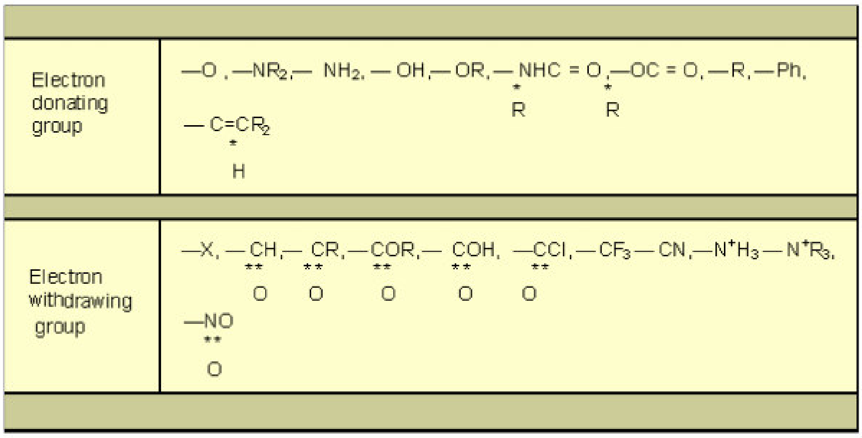


X = halogen

Common electron-withdrawing groups:
- Halogens
- Groups with an atom Y bearing a positive charge (δ^+ or +) bonded to the benzene ring.

Example of Electron Withdrawing

Table showing few electron donating and withdrawing groups



Electron donating group	$-O$, $-NR_2$, $-NH_2$, $-OH$, $-OR$, $-\underset{\substack{*\\ R}}{N}HC=O$, $-\underset{\substack{*\\ R}}{O}C=O$, $-R$, $-Ph$, $-\underset{\substack{*\\ H}}{C}=CR_2$
Electron withdrawing group	$-X$, $-\underset{\substack{**\\ O}}{C}H$, $-\underset{\substack{**\\ O}}{C}R$, $-\underset{\substack{**\\ O}}{C}OR$, $-\underset{\substack{**\\ O}}{C}OH$, $-\underset{\substack{**\\ O}}{C}Cl$, $-CF_3$ $-CN$, $-N^+H_3$ $-N^+R_3$, $-\underset{\substack{**\\ O}}{N}O$

Relative Reactivity of Substituent Benzene

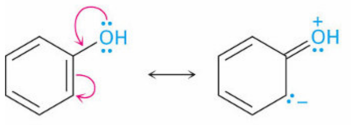
- 2 type of subs. Which affects reactivity of benzene ring:

(a) Activating subs. – activate ring (donate e)

(b) Deactivating subs – deactivate ring (withdraw e)

Activating subs

- Except alkyl group, all activating subs. donate e into the ring by resonance and withdraw e from the ring inductively.
- Example

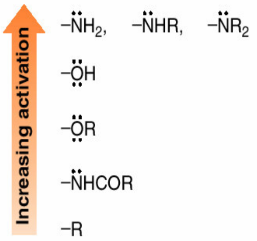


Resonance electron donation

All substituents under e donating group

[1] ortho, para directors and activators

- **Substituents that *activate* a benzene ring and direct substitution ortho and para.**



$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$

$-\ddot{\underset{..}{O}}H$

$-\ddot{\underset{..}{O}}R$

$-\ddot{N}HCOR$

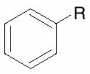
$-R$

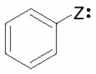
General structure

$-R$ or $-Z$:

- **Keep in mind that halogens are in a class by themselves.**
- **Also note that:**

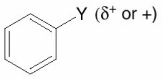
- All ortho, para directors are R groups or have a nonbonded electron pair on the atom bonded to the benzene ring.





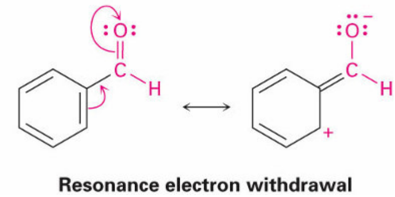
Z = N or O ⟶ The ring is **activated.**
Z = halogen ⟶ The ring is **deactivated.**

- All meta directors have a full or partial positive charge on the atom bonded to the benzene ring.



Deactivating subs

- Halogen are weakly deactivating subs. (they withdraw e inductively stronger than they can donate e resonance)
- All subs. that are strongly deactivating compare to halogen able to withdraw e both inductively and resonance.



Resonance electron withdrawal

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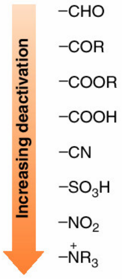
[2] ortho, para deactivators

- **Substituents that *deactivate* a benzene ring and direct substitution ortho and para.**

–F: –Cl: –Br: –I:

[3] meta directors

- **Substituents that direct substitution meta.**
- **All meta directors *deactivate* the ring.**



$-CHO$

$-COR$

$-COOR$

$-COOH$

$-CN$

$-SO_3H$

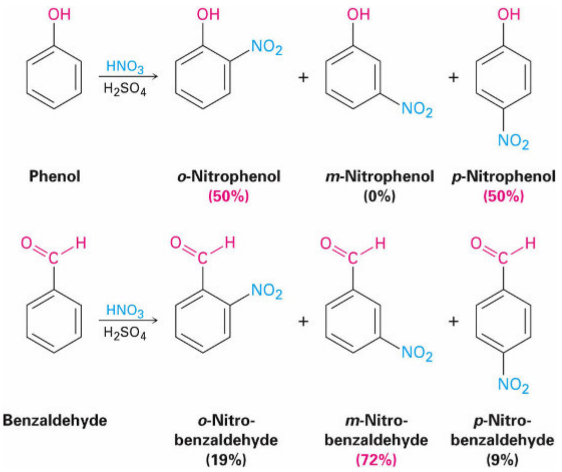
$-NO_2$

$-\overset{+}{N}R_3$

General structure
–Y (δ^+ or +)

Substituents affect the orientation of the reaction

- ☐ The three possible disubstituted products – ortho, meta, and para – are usually not formed in equal amounts
- ☐ The nature of the substituent on the ring determines the position of the second substitution



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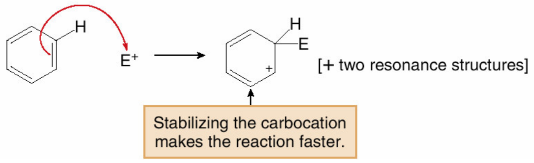
3 Group of Subs.

a. Activating subs.
b. Weakly deactivating subs.
c. Moderate deactivating / strongly deactivating subs.

- To understand how substituents activate or deactivate the ring, we must consider the first step in electrophilic aromatic substitution.
- The first step involves addition of the electrophile (E+) to form a resonance stabilized carbocation.
- The Hammond postulate makes it possible to predict the relative rate of the reaction by looking at the stability of the carbocation intermediate.

> - **The more stable the carbocation, the lower in energy the transition state that forms it, and the faster the reaction.**



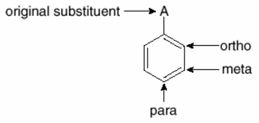
[+ two resonance structures]

Stabilizing the carbocation makes the reaction faster.

To evaluate the effects of a given substituent, we can use the following stepwise procedure:

How To Determine the Directing Effects of a Particular Substituent

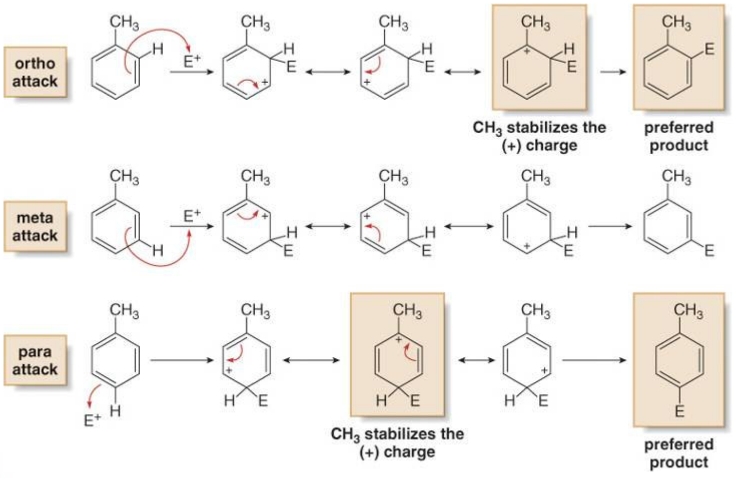
Step [1] Draw all resonance structures for the carbocation formed from attack of an electrophile E^+ at the ortho, meta, and para positions of a substituted benzene (C_6H_5-A).



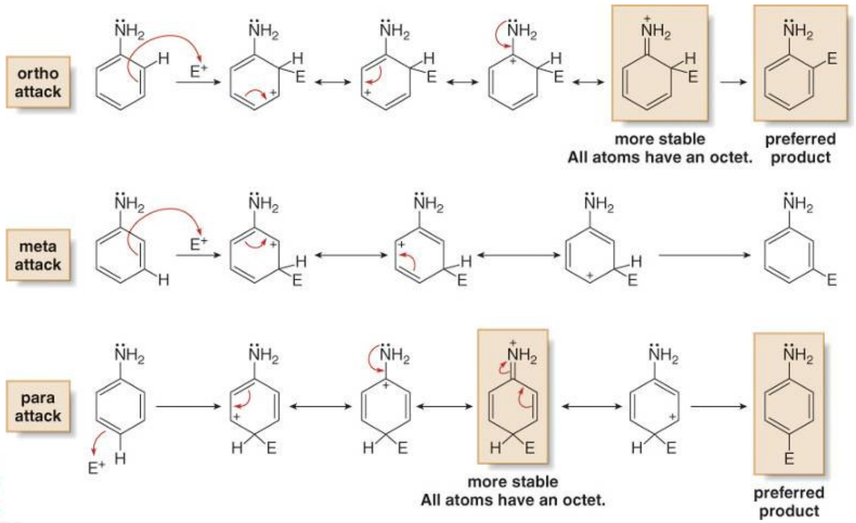
- There are at least three resonance structures for each site of reaction.
- Each resonance structure places a positive charge ortho or para to the new C – E bond.

Step [2] Evaluate the stability of the intermediate resonance structures. The electrophile attacks at those positions that give the most stable carbocation.

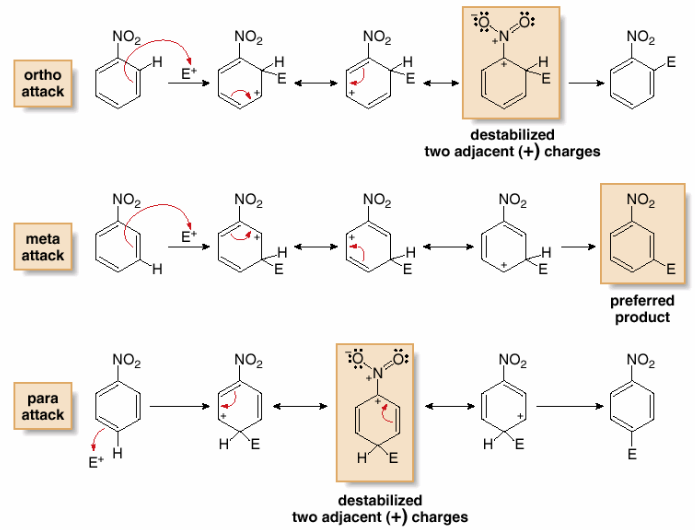
- A CH_3 group directs electrophilic attack ortho and para to itself because an electron-donating inductive effect stabilizes the carbocation intermediate.



- An NH_2 group directs electrophilic attack ortho and para to itself because the carbocation intermediate has additional resonance stabilization.

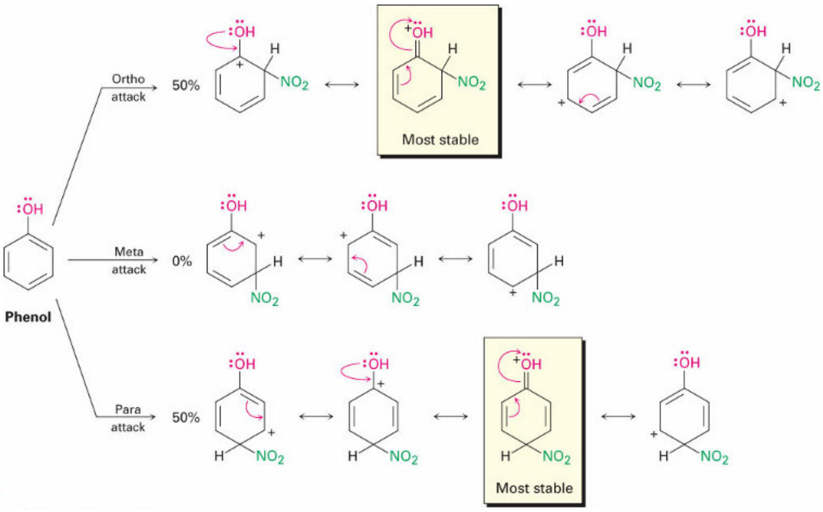


- With the NO_2 group (and all meta directors) meta attack occurs because attack at the ortho and para position gives a destabilized carbocation intermediate.

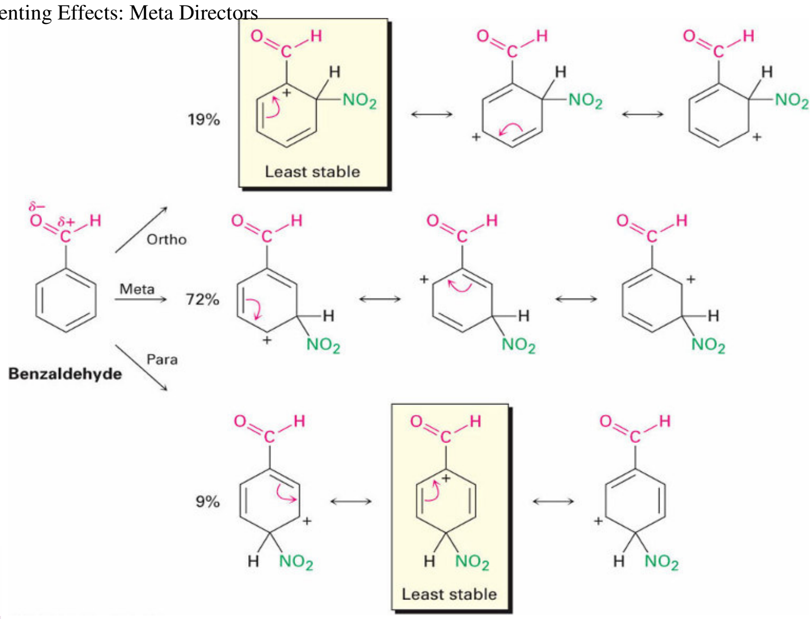


Orienting Effects: Ortho and Para Directors

- The ortho and para intermediates are more stable than the meta intermediate because they have more resonance forms

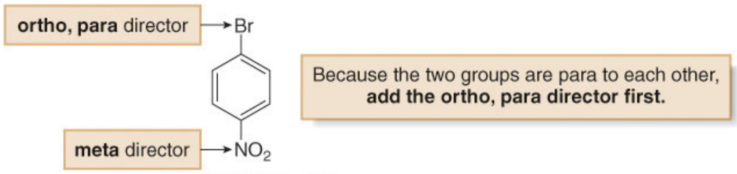


Orienting Effects: Meta Directors



Synthesis of Benzene Derivatives

In a disubstituted benzene, the directing effects indicate which substituent must be added to the ring first.



ortho, para director → Br

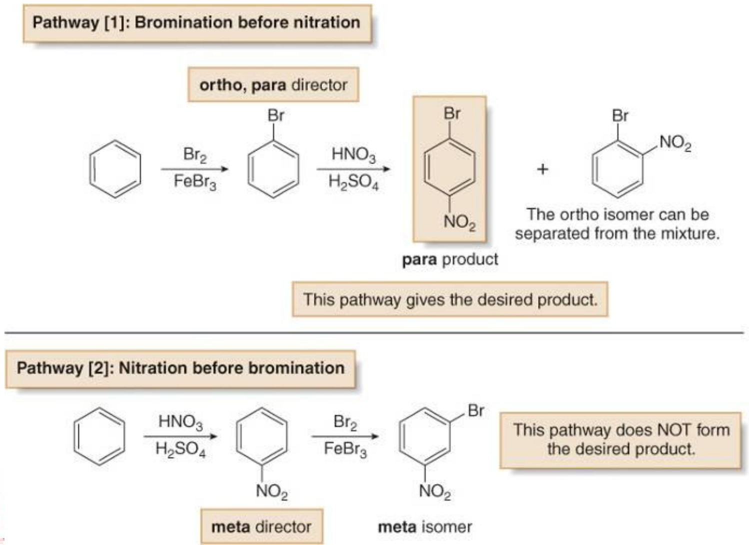
meta director → NO_2

Because the two groups are para to each other, **add the ortho, para director first.**

p-bromonitrobenzene

Let us consider the consequences of bromination first followed by nitration, and nitration first, followed by bromination.

Pathway I, in which bromination precedes nitration, yields the desired product. Pathway II yields the undesired meta isomer.



Pathway [1]: Bromination before nitration

ortho, para director

para product

The ortho isomer can be separated from the mixture.

This pathway gives the desired product.

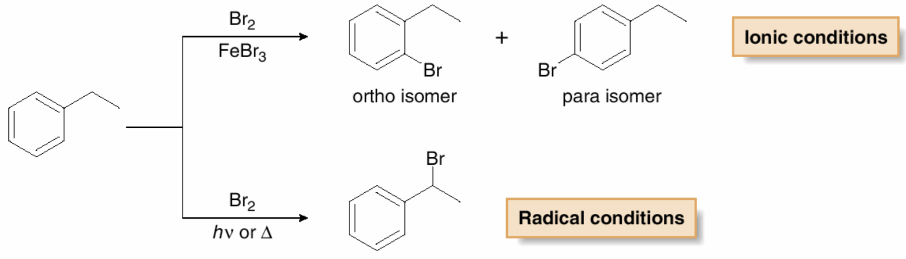
Pathway [2]: Nitration before bromination

This pathway does NOT form the desired product.

meta director

meta isomer

Note that alkyl benzenes undergo two different reactions depending on the reaction conditions:



- With Br_2 and $FeBr_3$ (ionic conditions), electrophilic aromatic substitution occurs, resulting in replacement of H by Br on the aromatic ring to form ortho and para isomers.
- With Br_2 and light or heat (radical conditions), substitution of H by Br occurs at the benzylic carbon of the alkyl group.